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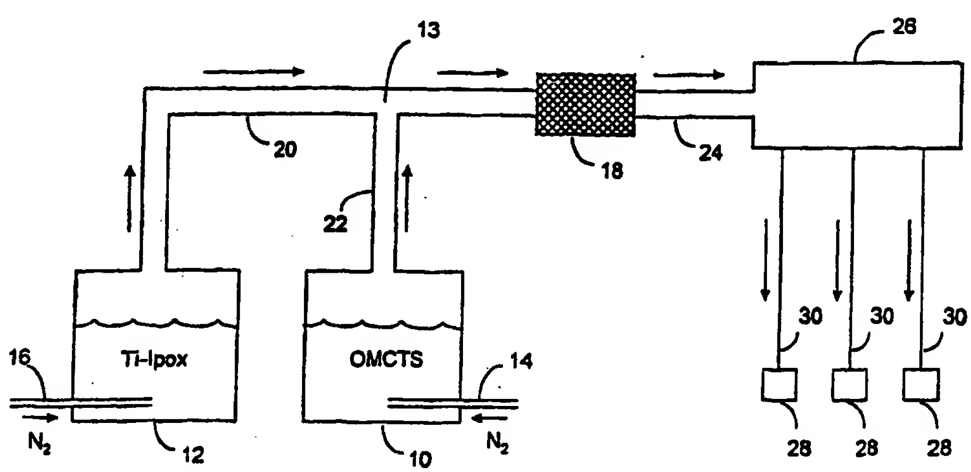
(54) Title: METHODS FOR MAKING ULTRA-LOW EXPANSION SILICA-TITANIA GLASSES



(57) Abstract

Ultra-low expansion silica-titania glasses are produced by flame deposition of a mixture of vaporized octamethylcyclotetrasiloxane (OMCTS) and vaporized titanium isopropoxide (Ti-Ipox). Ti-Ipox is vaporized by nitrogen bubbled from conduit (16) into tank (12) and OMCTS is vaporized by nitrogen bubbled from conduit (14) in tank (10). Before being mixed with the Ti-Ipox, the OMCTS is dried so that its water content is less than 2 ppm and preferably less than 1 ppm. In this way, the formation of a precipitate on the glass making equipment (e.g., burners (28), distribution manifold (26), static mixer (18), joint (13), and conduits (20, 22, 24 and 30)) is avoided. Such a precipitate if allowed to form will result in premature shutdown of the glass making process and can result in undesirable variations in the composition of the silica-titania glass being produced.

METHODS FOR MAKING ULTRA-LOW EXPANSION SILICA-TITANIA GLASSES

U.S. GOVERNMENT RIGHTS

The government of the United States of America has rights in this invention pursuant to Subcontract No. B299143 awarded by the Regent of the University of California under prime contract No. W-7405-ENG-48 awarded by the U.S. Department of Energy.

FIELD OF THE INVENTION

This invention relates to ultra-low expansion glasses composed of SiO_2 and TiO_2. More particularly, the invention relates to environmentally friendly methods for making such glasses.

BACKGROUND OF THE INVENTION

Historically, ultra-low expansion glasses composed of SiO_2 and TiO_2 have been made by flame hydrolysis (flame deposition) of $SiCl_4$ and $TiCl_4$. The deposition process is carried out in a furnace composed of a refractory crown, which carries a series of soot producing burners, and a refractory cup, which collects the soot produced by the burners to form a glass "boule." The TiO_2 concentration in the finished glass is typically in the 5-11% by weight range (e.g., approximately 7% by weight) and the glass has an expansion coefficient of less than $5x10^{-7}/°C$. See U.S. Patent No. 2,326,059.

$SiCl_4$ and $TiCl_4$ are clearly chlorine-containing compounds. When used to make glass, these raw materials result in the production of various chlorine-containing by-products, e.g., Cl_2 and HCl, which can cause environmental damage. Although these by-products can be collected by scrubbing the emission gases which exit the glass making furnace, such scrubbing is expensive and complicates the glass making process.

To avoid the production of chlorine-containing by-products, halide-free polymethylsiloxanes have been used in the production of silica-containing glasses. In particular, octamethylcyclotetrasiloxane (OMCTS)

has been used for this purpose. See Dobbins et al., U.S. Patent No. 5,043,002, and Blackwell et al., U.S. Patent No. 5,152,819, the contents of both of which are incorporated herein by reference.

Blackwell et al., U.S. Patent No. 5,154,744, the contents of which are also incorporated herein by reference, describes the production of titania-doped fused silica glass using OMCTS and a number of titanium-containing organic compounds, including titanium isopropoxide (Ti-Ipox). Significantly, with regard to the present invention, there is no disclosure in this patent that without special treatment, OMCTS cannot be used with Ti-Ipox in the commercial production of SiO_2-TiO_2 glasses and, in particular, the production of ultra-low expansion SiO_2-TiO_2 glasses.

SUMMARY OF THE INVENTION

In view of the foregoing state of the art, it is an object of the present invention to provide improved methods for producing ultra-low expansion glasses. In particular, it is an object of the invention to provide environmentally friendly methods for producing ultra-low expansion glasses composed of SiO_2 and TiO_2. It is a further object of the invention to provide methods for making OMCTS compatible with Ti-Ipox.

In accordance with the invention, it has been surprisingly found that: (1) Ti-Ipox is exceedingly sensitive to even the smallest amounts of water and/or hydroxyl groups in OMCTS; and (2) OMCTS as commercially supplied contains amounts of dissolved water and silanols (SiOH) well above the levels to which Ti-Ipox is sensitive, even though OMCTS is considered in the art to be a hydrophobic material, e.g., commercially available OMCTS typically has a water content of around 10 ppm but can have water levels as high as 200 ppm or even higher.

The sensitivity of Ti-Ipox to water/hydroxyl groups present in OMCTS can be best understood by reference to the apparatus of Figure 1. This figure shows storage tanks 10 and 12 for OMCTS and Ti-Ipox, respectively, each storage tank being equipped with appropriate heating equipment (not shown) for converting its contents into vapor form. An inert

gas, e.g., nitrogen, is supplied to tanks 10 and 12 through feed lines 14 and 16, respectively, and serves to carry vaporized OMCTS and vaporized Ti-Ipox to static mixer 18 by means of conduits 20 and 22. From static mixer 18, the mixed vapors pass through conduit 24 to distribution manifold 26 and from there to burners 28 by means of conduits 30.

In this arrangement, the OMCTS and Ti-Ipox vapors are only in contact between joint 13 and burners 28. This corresponds to a contact time of only a few seconds. Yet, in accordance with the invention, it was discovered that even this limited amount of exposure of Ti-Ipox to the water/hydroxyl groups in OMCTS results in substantial impairment of the glass making process. In particular, the water/hydroxyl groups in OMCTS were found to hydrolyze the Ti-Ipox resulting in the formation of a white precipitate at all points downstream of joint 13. This precipitate, which is believed to be TiO_2, accumulates on, among other things, burners 28 resulting in pressure increases in distribution manifold 26 and deviations in the composition of the boule. As a result, frequent shutdowns of the process are required for precipitate removal so that only boules of a limited size can be made which, in many cases, are too small for use in making desired products, e.g., are too small to make low expansion optical mirrors having large diameters. The presence of the precipitate in the glass making apparatus can also result in off-spec material, e.g., materials having elevated expansion coefficients, thus reducing the overall yield of the process.

To solve this problem, the invention in accordance with certain of its aspects provides a method for producing a silica-titania glass which comprises the steps of:

(a) producing a first gas stream which comprises OMCTS in vapor form, e.g., an OMCTS/N_2 gas stream carried by conduit 22;

(b) producing a second gas stream comprising Ti-Ipox in vapor form, e.g., an Ti-Ipox/N_2 gas stream carried by conduit 20;

(c) mixing the first and second gas streams to form a third gas stream, e.g., the mixing of the first gas stream in conduit 22 with the second gas stream in conduit 20 at joint 13 and in static mixer 18 to produce a mixed gas stream (the third gas stream) in conduit 24;

(d) forming soot particles from the third gas stream using at least one burner, e.g., forming soot particles from the gas stream in conduit 24 by means of distribution manifold 26, conduits 30, and burners 28; and

(e) producing the desired silica-titania glass from the soot particles, e.g., by collecting the soot particles produced by burners 28 to form a boule, with the boule being consolidated as the soot particles are collected or alternatively, but less preferred, after the particles are collected;

wherein the concentration of water and/or hydroxyl groups in the first gas stream is sufficiently low so that mixing of the first and second gas streams does not result in the formation of a substantial amount of a precipitate as a result of hydrolysis of Ti-Ipox. As used herein, a "substantial amount" of precipitate is an amount which necessitates premature shut down of the glass making process for precipitate removal before a desired quantity of glass has been produced.

In certain preferred embodiments of the invention, the concentration of water in the OMCTS prior to its incorporation in the first gas stream is less than 2 ppm and, most preferably, less than 1 ppm. Such a low concentration of water is preferably achieved by pre-drying the OMCTS before it is introduced into tank 10. The inert gas provided to tank 10 by conduit 14 must also be dry so that water is not reintroduced into the OMCTS. Similarly, the inert gas provided to tank 12 by conduit 16 must also be dry.

Although OMCTS and Ti-Ipox are the preferred starting materials for producing silica-titania glasses, other halide-free compounds can be

used in the practice of the invention. For example, rather than OMCTS, other polymethylsiloxanes or, more generally, other halide-free, silicon-containing compounds which can be converted through thermal decomposition with oxidation or flame hydrolysis to SiO_2 can be used in the practice of the invention. Similarly, rather than Ti-Ipox, other titanium-containing organic compounds or, more generally, other halide-free, titanium-containing compounds which are sensitive to water and/or hydroxyl groups and which can be converted through thermal decomposition with oxidation or flame hydrolysis to TiO_2 can be used. Discussions of such alternative compounds can be found in U.S. Patents Nos. 5,043,002, 5,152,819, and 5,154,744, referred to above.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of apparatus which can be used in the practice of the invention to produce silica-titania glasses.

Figure 2 is a schematic diagram of apparatus which can be used to produce "dry" OMCTS.

The foregoing drawings, which are incorporated in and constitute part of the specification, illustrate the preferred embodiments of the invention, and together with the description, serve to explain the principles of the invention. It is to be understood, of course, that both the drawings and the description are explanatory only and are not restrictive of the invention. The drawings are not intended to indicate scale or relative proportions of the elements shown therein.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Figure 2 shows suitable equipment for producing an OMCTS feedstock having a low water content. As shown in this figure, OMCTS which is to be dried (the "wet" OMCTS) is introduced into tank 32 through conduit 34 which is equipped with shut off valve 36. The wet OMCTS is heated to a temperature of, for example, 140°F, after which dry nitrogen is pumped into the tank through conduit 38. Conduit 38 can be equipped with a sparger so as to produce numerous small bubbles which flow upward

through the wet OMCTS. A nitrogen flow rate of 12.5 scfm has been found suitable to dry approximately 300 gallons of OMCTS in about 3.5 hours.

The heating of the OMCTS is preferably performed by hot oil tracing of tank 32. Although electric heating can be used, hot oil heating is preferred since it reduces the chances of hot spots along the surface of the tank which can result in undesirable polymerization of the OMCTS. Even with hot oil heating, the temperatures of the OMCTS and of the hot oil need to be monitored to avoid excessive heating and thus polymerization of the OMCTS. Because the vapor pressure of water is substantially greater than that of OMCTS, the temperature of the wet OMCTS does not have to be raised above 212°F to achieve effective water removal but only to a temperature of around 140°F.

As dry nitrogen from conduit 38 passes through the heated OMCTS, it picks up water vapor which is carried out of the tank through conduit 40, leaving behind drier OMCTS. As the drying process proceeds, the water level remaining in the OMCTS is monitored by means of monitoring circuit 46 which includes pump 42 and moisture sensor 44. Moisture sensor 44 can, for example, be a PANAMETRICS brand sensor manufactured by Panametrics Incorporated, Waltham, MA. Although this sensor gives somewhat qualitative results, it has been found to work successfully in practice.

When the concentration of water in the OMCTS drops to below 1 ppm (e.g., to a level of 0.8 ppm) and remains at that concentration for a period of, for example, one hour, the flow of nitrogen is shut off and the dried OMCTS is transferred to storage tank 50 using pump 48. By means of conduit 52, a blanket of dry nitrogen is maintained over the "dry" OMCTS as it is being pumped into tank 50, as well as during storage in that tank. When needed in the glass making process, the dry OMCTS is transferred to tank 10 of Figure 1 using outlet conduit 54 of tank 50 and an appropriate inlet conduit (not shown) to tank 10.

The apparatus of Figures 1 and 2 is preferably made of stainless steel, e.g., 304L SS, except for conduits 30 in Figure 1 which are preferably PFA TEFLON. Tanks 10 and 12 in Figure 1, as well as the conduits shown in that figure, are preferably hot oil traced. As discussed above, tank 32 in Figure 2 is also hot oil traced, as are the various conduits associated with that tank which carry OMCTS.

In practice, the difference between using dry OMCTS versus using wet OMCTS has been found to be dramatic. Thus, using wet OMCTS, the pressure in the distribution manifold 26 of Figure 1 was found to rise from 15 inches of water to 65 inches of water in two hours as a result of precipitate buildup in the system. When dry OMCTS was used, the pressure increased by only 1 inch of water over a period of 160 hours, thus allowing full sized boules of ultra low expansion silica-titania glass to be produced.

Although specific embodiments of the invention have been described and illustrated, it is to be understood that modifications can be made without departing from the invention's spirit and scope. For example, equipment other than that illustrated in Figure 2, e.g., equipment which operates on a continuous as opposed to a batch basis, can be used to dry the OMCTS prior to its vaporization and mixture with vaporized Ti-Ipox. Similarly, although the invention has been described in terms of producing glass boules of ultra-low expansion silica-titania glasses, it can also be used in the production of other silica glasses which contain titanium. For example, the invention can be used in the preparation of titanium-doped preforms from which optical waveguide fibers can be drawn.

A variety of other modifications which do not depart from the scope and spirit of the invention will be evident to persons of ordinary skill in the art from the disclosure herein. The following claims are intended to cover the specific embodiments set forth herein as well as such modifications, variations, and equivalents.

What is claimed is:

1. A method for producing a silica-titania glass comprising the steps of:

(a) producing a first gas stream comprising a halide-free, silicon-containing compound in vapor form;

(b) producing a second gas stream comprising a halide-free, titanium-containing compound in vapor form, said halide-free, titanium-containing compound forming a precipitate in the presence of water and/or hydroxyl groups;

(c) mixing the first and second gas streams to form a third gas stream;

(d) forming soot particles from the third gas stream using at least one burner; and

(e) producing the silica-titania glass from the soot particles;

wherein the concentration of water and/or hydroxyl groups in the first gas stream is sufficiently low so that mixing of the first and second gas streams does not result in the formation of substantial amounts of said precipitate.

2. The method of Claim 1 wherein step (a) comprises drying the halide-free, silicon-containing compound.

3. The method of Claim 1 wherein the concentration of water in the halide-free, silicon-containing compound is less than 2 ppm.

4. The method of Claim 1 wherein the concentration of water in the halide-free, silicon-containing compound is less than 1 ppm.

5. The method of Claim 1 wherein the halide-free, silicon-containing compound is a halide-free polymethylsiloxane.

6. The method of Claim 5 wherein the halide-free, silicon-containing compound is octamethylcyclotetrasiloxane.

7. The method of Claim 1 wherein the halide-free, titanium-containing compound is a titanium-containing organic compound.

8. The method of Claim 7 wherein the titanium-containing organic compound is titanium isopropoxide.

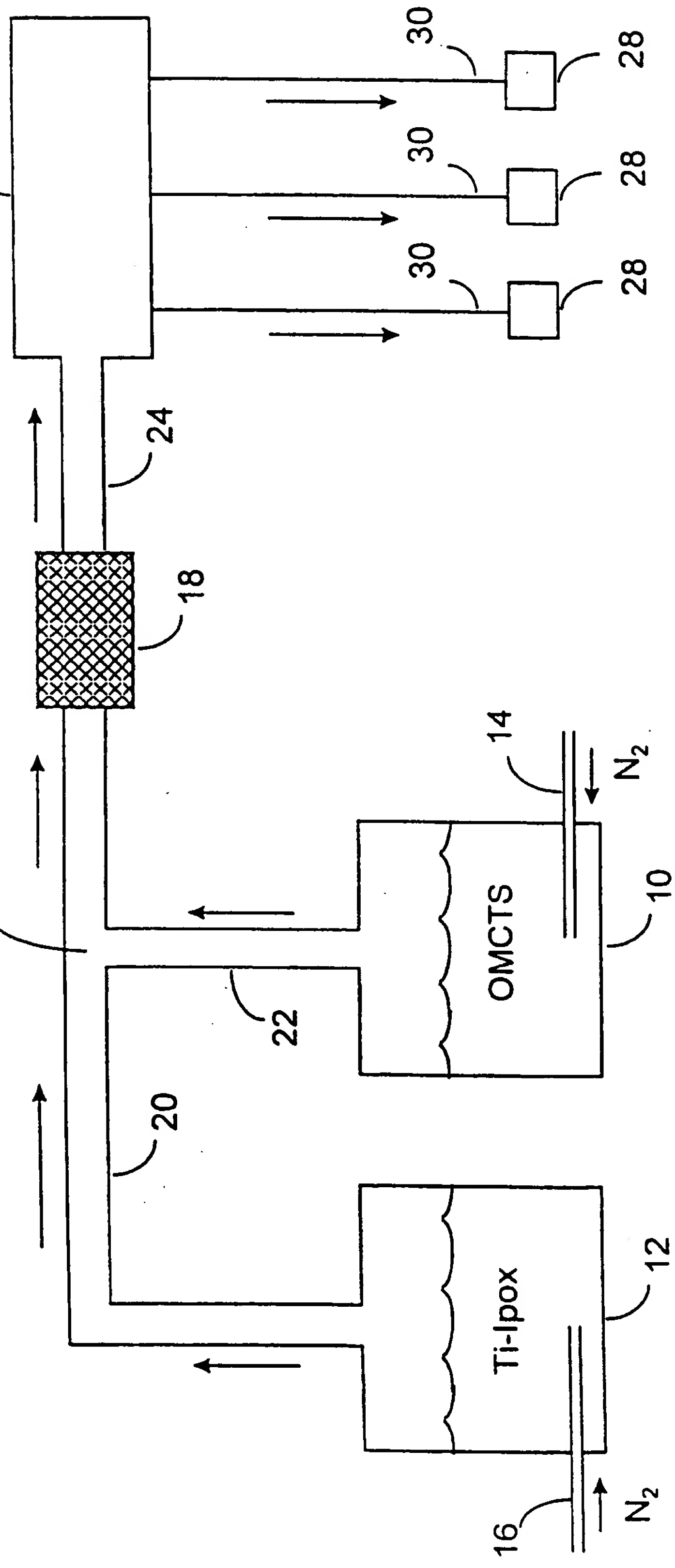


Fig. 1

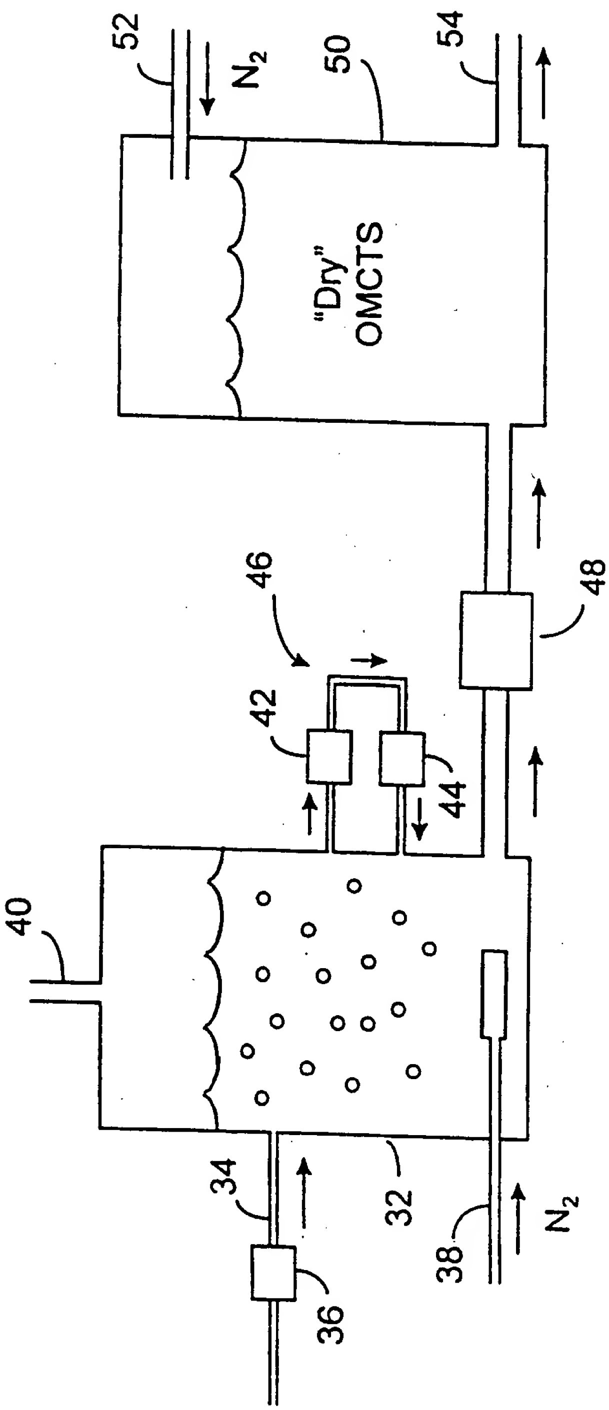


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/08777

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C03B 8/04, 20/00
US CL :65/17.4, 414

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 65/17.4, 413, 414, 422, 426; 427/167, 452; 423/336

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X --- P, Y	WO 98/27018 (BOEK ET AL) 25 June 1998, claims 4-6.	1 and 5-8 --- 2-4
X --- Y	US 5,154,744 A (BLACKWELL ET AL) 13 October 1992, col. 2, line 60 to col. 7, line 22.	1 and 5-8 --- 2-4
Y	US 5,451,390 A (HARTMANN ET AL) 19 September 1995, entire patent.	2-4
A	US 5,043,002 A (DOBBINS ET AL) 27 August 1991.	1-8
A	US 5,152,819 A (BLACKWELL ET AL) 06 October 1992.	1-8

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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09 JUNE 1999	29 JUN 1999

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B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS, STN

search terms: silica, titania, sio2, tio2, titanium oxide, omcts, ti (1w) ipox, octamethylcyclotetrasiloxane, titanium isopropoxide, hydrolysis or soot, water or hydroxyl?, remov? or free.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/08777

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 4-74728 A (SUMIMOTO ELECTRIC IND CO) 10 March 1992.	1-8
A	JP 6-160657 A (MITSUBISHI ELECTRIC CORP) 07 June 1994.	1-8

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